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Relationship between Mn Oxidation State Changes and Oxygen Reduction Activity in (La,Ca)MnO₃ as Probed by *In Situ* XAS and XES

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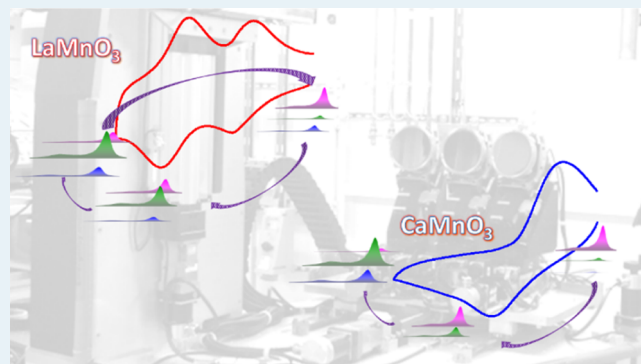


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ABSTRACT: *In situ* X-ray absorption and emission spectroscopies (XAS and XES) are used to provide details regarding the role of the accessibility and extent of redox activity of the Mn ions in determining the oxygen reduction activity of LaMnO₃ and CaMnO₃, with X-ray absorption near-edge structure (XANES) providing the average oxidation state, extended X-ray absorption fine structure (EXAFS) providing the local coordination environment, and XES providing the population ratios of the Mn²⁺, Mn³⁺, and Mn⁴⁺ sites as a function of the applied potential. For LaMnO₃, XANES and XES show that Mn³⁺ is formed, but Mn⁴⁺ ions are retained, which leads to the 4e[−] reduction between 0.85 and 0.6 V. At more negative potentials, down to 0.2 V, EXAFS confirms an increase in oxygen vacancies as evidenced by changes in the Mn–O coordination distance and number, while XES shows that the Mn³⁺ to Mn⁴⁺ ratio increases. For CaMnO₃, XANES and XES show the formation of both Mn³⁺ and Mn²⁺ as the potential is made more negative, with little retention of Mn⁴⁺ at 0.2 V. The EXAFS for CaMnO₃ also indicates the formation of oxygen vacancies, but in contrast to LaMnO₃, this is accompanied by loss of the perovskite structure leading to structural collapse. The results presented have implications in terms of understanding of both the pseudocapacitive response of Mn oxide electrocatalysts and the processes behind degradation of the activity of the materials.



KEYWORDS: perovskite oxides, oxygen reduction reaction, X-ray absorption/emission, LaMnO₃, CaMnO₃, manganese redox

INTRODUCTION

The increased interest in electrochemical energy-storage/conversion systems such as metal-air batteries, fuel cells, and electrolyzers arising from the interest in electrification of energy supply and distribution has motivated many studies of oxygen reduction and evolution reaction (ORR and OER) electrocatalysts.^{1,2} The development of more efficient and stable materials is a critical step for the final introduction of these devices in the market. Platinum-based catalysts and IrO₂ remain as benchmark materials for the ORR and OER, respectively, in acidic and alkaline environments,^{3,4} but significant efforts have also been focused on earth-abundant and low-cost materials.^{5,6} A growing number of publications on the electrocatalytic properties of Co-, Ni-, and Mn-containing spinel and perovskite oxides have emerged in recent years.^{7,8} The mixed valency of individual elements in the parent materials, further complicated under operating conditions, makes the identification of composition–activity relationships more difficult for such materials.⁹ A deeper understanding of the contributions of each component ion to the activity is required to more fully develop such relationships and enable the design of more active/stable electrocatalysts.^{9,10}

Mn-based oxides are among the most active catalysts toward the oxygen reduction reaction (ORR) in alkaline solutions. After the seminal work by Bockris and Otagawa¹¹ and the elegant work of Suntivich *et al.* on perovskite oxides,¹² the prevailing view is that a single electron occupancy of the e_g orbital of the metal at the B-site of the perovskite structure represents the optimum configuration for oxygen electrocatalysis. This trend implies that LaMnO_{3+δ} (e_g ~ 1) should be more active than CaMnO₃ (e_g ~ 0), suggesting that there is an optimal oxidation state of the active metal. However, numerous works have shown that the orbital occupancy on Mn states changes in the potential range relevant to the ORR. For example, our recent works on perovskite nanoparticles demonstrated that changes in the redox state of the B-site at Mn-based perovskites are directly linked to their activity toward the ORR.^{13,14} Studies on thin films have

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provided evidence that Mn^{3+} or a mixed valence $\text{Mn}^{3+}/\text{Mn}^{4+}$ corresponds to the active material.^{15–18} Ryabova *et al.* proposed that the potential of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox transition could be used as a descriptor for the ORR activity,¹⁹ with the highest activity corresponding to the catalyst with the more positive redox potential.

Understanding the ORR mechanism at such complex materials requires direct information regarding the changes in the orbital occupancy of the Mn sites that can only be achieved using *in situ* characterization techniques. *In situ* X-ray absorption near-edge structure (XANES) studies enable identification of the oxidation states of the metal atoms, while the extended X-ray absorption fine structure (EXAFS) data enable the study of the accompanying change in oxygen coordination. For example, Gorlin *et al.*²⁰ and Risch *et al.*²¹ concluded that manganese was reduced below Mn^{3+} and contained significant fractions of Mn^{2+} by looking at the Mn K-edge and Mn L-edge, respectively, in agreement with previous studies by Lima *et al.* at the Mn K-edge.²² Although such X-ray absorption measurements provide element-specific information, they only enable identification of the average oxidation state of the absorbing atom owing to the energy resolution of the spectra.

The resolution of the XANES can be improved by use of a high-energy-resolution fluorescence detection (HERFD) spectrometer, which enhances the pre-edge features and detail at the edge by overcoming the core-hole lifetime broadening of the 1s hole present in conventional K-edge XANES.^{23–25} The fractional contributions of the valence states to the average oxidation state can be obtained by analysis of the X-ray emission spectroscopy (XES) spectra and in particular the $\text{K}\beta$ emission lines ($3p \rightarrow 1s$), comprising the main $\text{K}\beta_{1,3}$ and the $\text{K}\beta'$ satellite peaks which are sensitive to the 3d spin state of the emitting atom.²⁶ Traulsen *et al.* employed these methods to study the polarization-induced changes to the oxidation state of Mn for a $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3+\delta}$ solid-oxide fuel cell electrocatalyst under *operando* conditions at 500 °C, demonstrating that the average Mn oxidation state decreased from +3.4 at an open circuit to +3.2, corresponding to 34% Mn^{4+} , 49% Mn^{3+} , and 17% Mn^{2+} , at –800 mV applied potential.²⁷ Here, we implement electrochemical *in situ* XES and EXAFS to unravel the complex correlation between orbital occupancy of Mn sites and their electrocatalytic activities toward the ORR. For the first time, we demonstrate that electrochemical signatures associated with LaMnO_3 at potential close to ORR formal potential are linked to an increase in the orbital occupancy of Mn 3d sites as well as changes in the Mn–O bond distance and coordination numbers. XES enables visualization of the changes in oxidation states in terms of the population ratio of Mn^{3+} (d^4) and Mn^{4+} (d^3) states. These changes are observed at significantly more negative potential in the case of CaMnO_3 , which is consistent with their lower activity toward the $4e^-$ ORR. Furthermore, we also observe that the structural integrity of CaMnO_3 is significantly more compromised upon potential cycling in comparison with LaMnO_3 .

RESULTS

Electrocatalytic Behavior of (La,Ca) MnO_3 Oxides.

Figure 1 shows the electrochemical response of LaMnO_3 and CaMnO_3 in Ar-saturated (a) and O_2 -saturated (b) 0.1 M KOH solution at 0.010 V s^{-1} for electrodes with the same mass of the oxides loaded onto the glassy carbon of a rotating disk electrode. The voltammogram (Figure 1a) of LaMnO_3 in the Ar-saturated electrolyte features two cathodic reduction peaks, which have

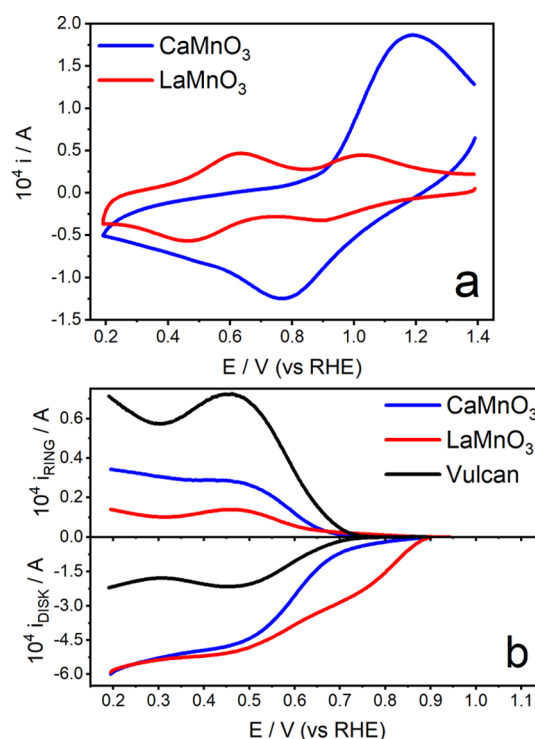


Figure 1. (a) Cyclic voltammograms of the LaMnO_3 and CaMnO_3 nanoparticles in Ar-saturated 0.1 M KOH solution at 0.010 V s^{-1} . (b) Rotating ring-disk electrode (RRDE) responses at 1600 rpm in O_2 saturated 0.1 M KOH at 0.010 V s^{-1} . The Pt ring was held at a constant potential of 1.10 V. Oxide nanoparticles were supported on a Vulcan layer ($50 \mu\text{g cm}^{-2}$) with a total oxide content of $250 \mu\text{g cm}^{-2}$. Data for the carbon electrode were $50 \mu\text{g cm}^{-2}$.

previously been attributed to the formation of a partially reduced state, followed by reduction to Mn^{2+} .^{28–31} The corresponding voltammogram of CaMnO_3 is characterized by a broad reduction peak centered at 0.80 V versus RHE (reversible hydrogen electrode, against which all potentials in this manuscript are reported) previously ascribed to the reduction of Mn^{4+} to Mn^{2+} .^{30,31} A small feature at ~0.5 V superimposed on the main broad voltammetric peak is also observed, which may suggest the presence of Mn^{3+} sites. An increase in current and thus in the charge involved in redox processes is observed for CaMnO_3 compared to that for LaMnO_3 , indicating that a larger number of Mn atoms change the oxidation state or that the change in the oxidation state for those Mn atoms that are active is larger within the potential window under study.

Figure 1b shows the disk (i_{DISK} , bottom panel) and ring (i_{RING} , top panel) currents obtained at 1600 rpm and 0.010 V s^{-1} in an O_2 -saturated 0.1 M KOH solution for LaMnO_3 and CaMnO_3 in comparison with an electrode just containing Vulcan carbon. The ORR onset potential is significantly more positive than that for the Vulcan support (*ca.* 0.7 V, see black curve in Figure 1), confirming that the reaction at potentials greater than 0.7 V takes place at the oxide particles. LaMnO_3 presents the most positive onset potential, while CaMnO_3 requires a higher overpotential to initiate the reaction. Substantial peroxide detection at the ring electrode is only observed at potentials more negative than 0.7 V, indicating that the Vulcan carbon may contribute to the partial reduction of O_2 to hydrogen peroxide. However, as differences are observed between the LaMnO_3 and CaMnO_3 catalysts at potentials below 0.7 V, the $4e^-$ reduction is still taking place on the oxide. The calculated peroxide yields are

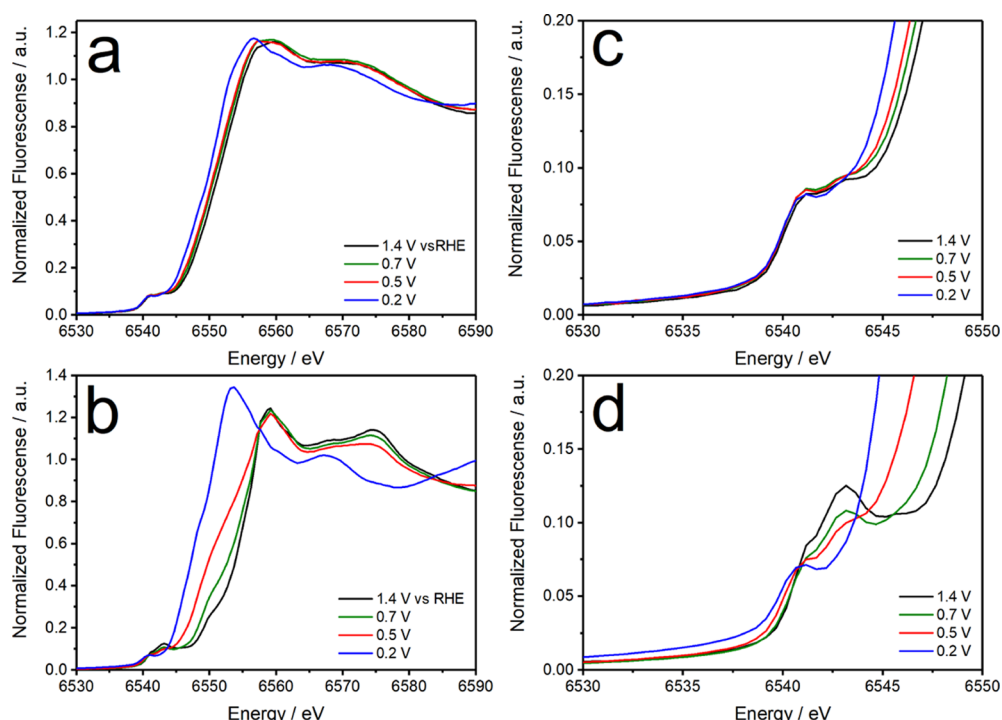


Figure 2. XANES spectra (a,b) and corresponding pre-edge regions (c,d) of the spectra at the Mn K-edge for LaMnO₃ (a,c) and CaMnO₃ (b,d) perovskite electrodes recorded at different applied potentials. Data collected in N₂-purged 0.1 M KOH.

provided as a function of the electrode potential in Figure S1. Comparing Figure 1a,b, we note that it is not until the first redox process occurs that the electrodes start generating peroxide.

In Situ XAS and XES Studies. *In situ* XAS spectra were collected in standard fluorescence mode using the SAMBA beamline at SOLEIL while applying potentials relevant to the ORR, from 1.4 V to 0.2 V *versus* RHE in N₂-purged 0.1 M KOH. Figure 2 shows the XANES spectra of the LaMnO₃ (a) and CaMnO₃ (b) catalysts. For LaMnO₃ at 0.2 V, the edge position (determined at the half of the edge step) is shifted to lower energy by 1.2 eV relative to the spectrum at the starting potential (1.4 V), whereas for CaMnO₃ at 0.2 V, the edge is shifted by 6.7 eV toward lower energy compared to the starting potential. This difference is greater than the 4 eV observed between MnO₂ and Mn₂O₃ standards (Figure S2), corresponding to the Mn⁴⁺ and Mn³⁺ oxidation states, respectively. It is interesting to notice that for CaMnO₃, the position of the maximum of the white line (defined as the maximum of the rising edge) also changes at 0.2 V compared to that at 1.4 V. The average Mn oxidation state can be estimated from the edge position by reference to a calibration plot generated from the reference samples, as shown in Figure S3. The oxidation state of the LaMnO₃ sample determined in this manner does not show much variation with potential, +3.7 at 1.4 V going to +3.1 at 0.2 V, while that of CaMnO₃ shows a much more significant shift from +4.7 at 1.4 V to +2.6 at 0.2 V. However, this method is rather approximate and can yield misleading results as the edge features of Mn are also dependent on the geometry and ligand environment.^{32,33} The average Mn oxidation state or number of unoccupied 3d states is more frequently probed by examination of the position of the pre-edge peak (1s → 3d) in the XANES (Figure 3c,d) following the approach by Croft *et al.*³⁴ The broadening and low intensity of the pre-edge features in the spectra obtained under *in situ* conditions prevents a reliable analysis of the changes in the oxidation state from these conventionally collected XANES

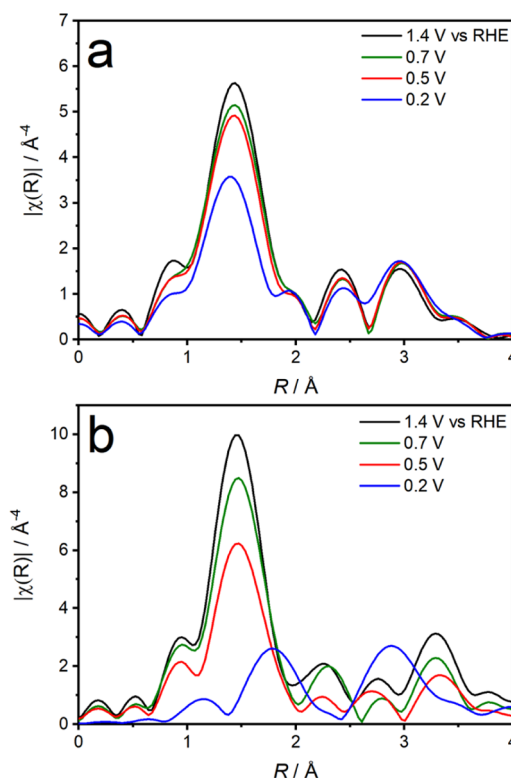


Figure 3. Fourier transforms of the k^3 -weighted Mn K-edge EXAFS of LaMnO₃ (a) and CaMnO₃ (b) at different potentials. The EXAFS data and fits for the first coordination shell in both k - and R -space are shown in Figure S7 and Table S4. Data recorded in N₂-purged 0.1 M KOH at room temperature. LaMnO₃: $2.6 < k < 10.9 \text{ \AA}^{-1}$; $1.1 < R < 2.2 \text{ \AA}$. CaMnO₃: $2.5 < k < 10.1 \text{ \AA}^{-1}$; $1.0 < R < 2.2 \text{ \AA}$.

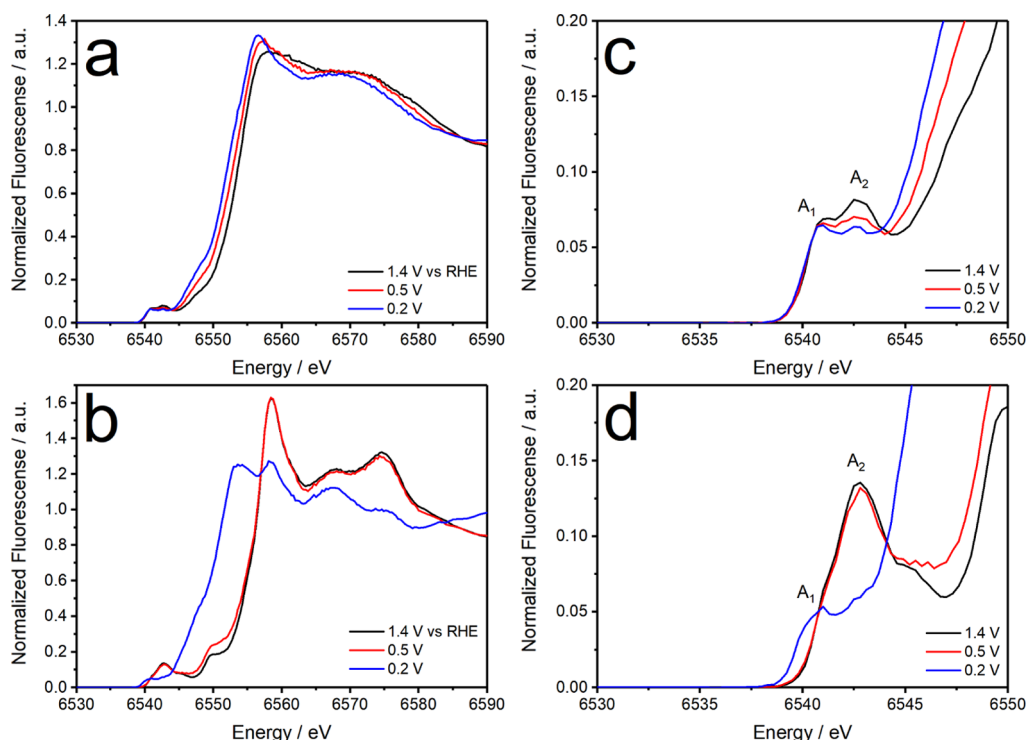


Figure 4. HERFD-XANES spectra (a,b) and corresponding pre-edge regions (c,d) obtained at the maximum of the $K\beta_{1,3}$ line of LaMnO₃ (a,c) and CaMnO₃ (b,d) as a function of the applied potential. Data recorded in N₂-purged 0.1 M KOH at room temperature.

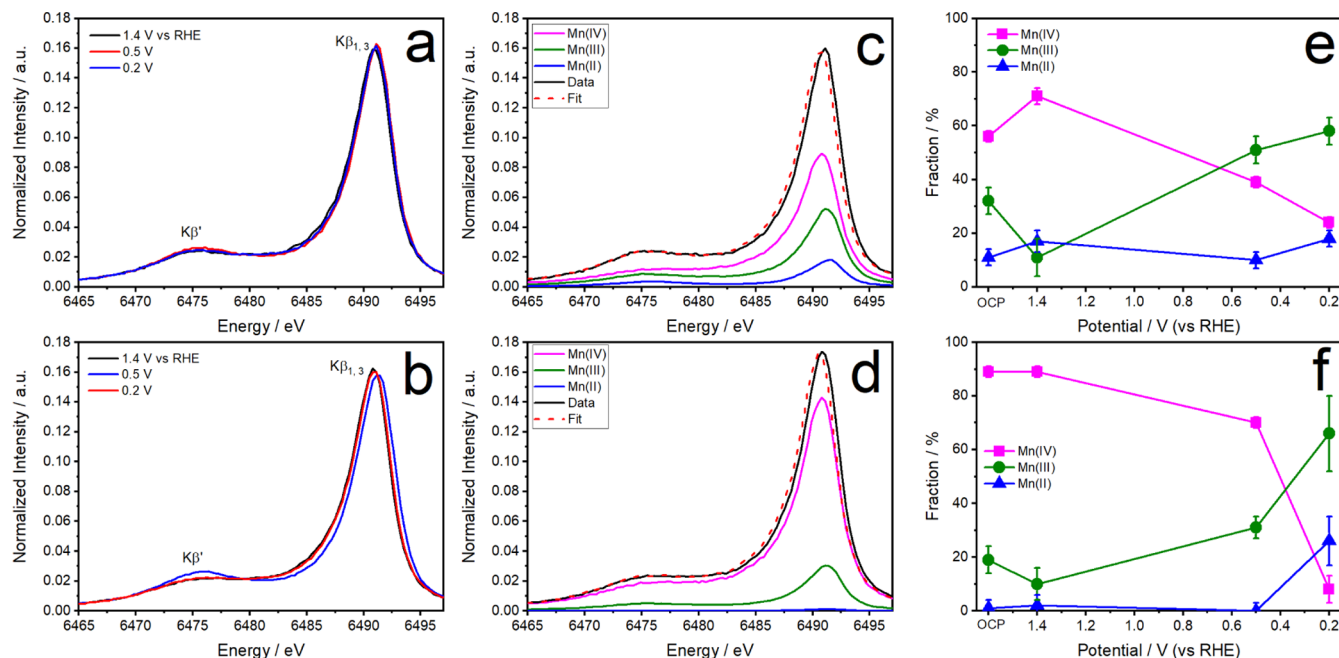


Figure 5. Normalized Mn $K\beta$ XES spectra measured at 100 eV from the absorption edge for LaMnO₃ (a) and CaMnO₃ (b) at different applied potentials. Linear combination of the normalized Mn $K\beta$ XES spectra for LaMnO₃ (c) and CaMnO₃ (d) for the electrodes inside the cell but without any applied potential (OCP). Percentage of the different cation species for LaMnO₃ (e) and CaMnO₃ (f) at the different potentials under study obtained by linear combination fitting of the XES data.

data. Nevertheless, very little change in the position of the pre-edge peak was observed for LaMnO₃ indicating only a small decrease in the average Mn oxidation state, while a more significant change is observed for the CaMnO₃ electrode.

Figure 3a,b shows the comparison between the Fourier transforms (FTs) of the EXAFS data at different potentials for LaMnO₃ and CaMnO₃. LaMnO₃ shows a decrease in amplitude

for the first shell and a slight compression of the Mn–O bond at 0.2 V. In the case of CaMnO₃, the change with potential is much more pronounced with an expansion of the first peak to 1.8 Å and a contraction of the second shell to 2.9 Å at 0.2 V, revealing that the coordination sphere of Mn and thus the (crystal) structure change with the applied potential. Although the EXAFS of the CaMnO₃ dry electrode and immersed electrode at

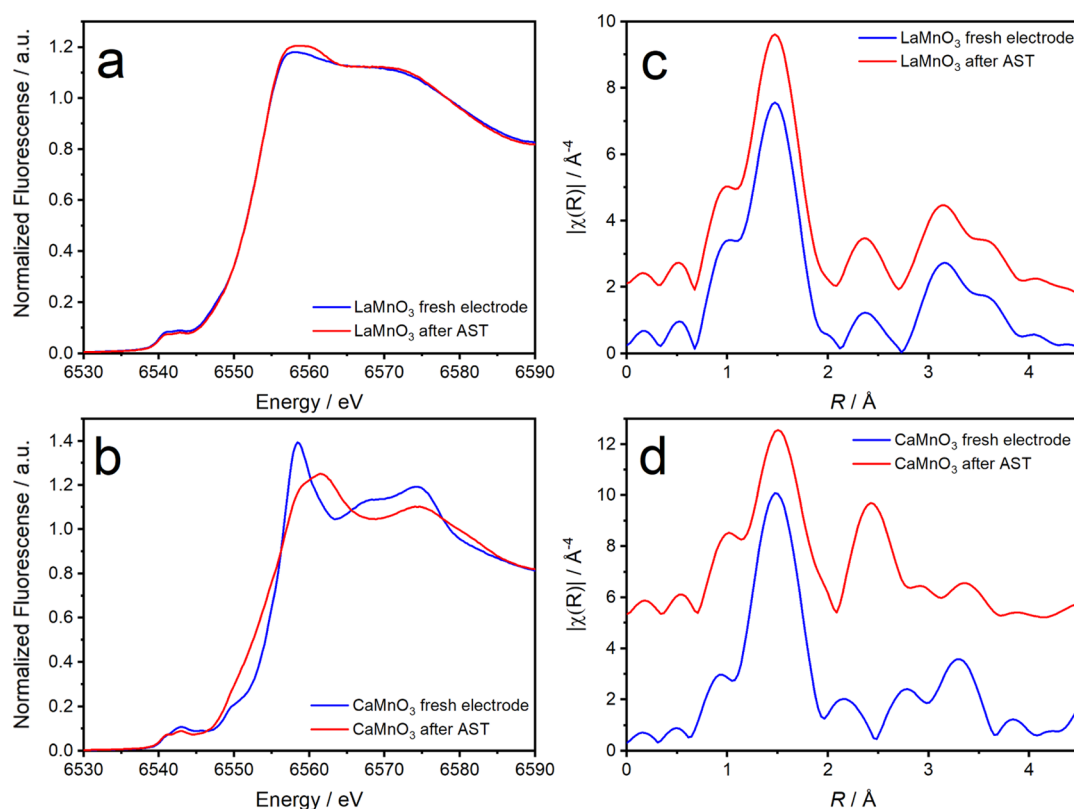


Figure 6. XANES spectra (a,b) and corresponding Fourier transforms of the k^3 -weighted EXAFS (c,d) of the spectra at the Mn K-edge for LaMnO₃ (a,c) and CaMnO₃ (b,d) perovskite electrodes recorded before and after the accelerated stress test.

the starting potential of 1.4 V can still be fitted using the same structure as for the *ex situ* pellet (pellet spectra and fits provided in Figure S4 and Table S1; that for the dry electrodes in Figure S5 and Table S2; and at 1.4 V in Figure S6 and Table S3), a decrease in the amplitude of the first peak in the Fourier transforms corresponding to Mn–O coordination is observed as the potential is made more negative (Figure S7 and Table S4), which is attributed to the creation of oxygen vacancies. For LaMnO₃, the higher-shell structure of the perovskite is retained upon the formation of oxygen vacancies as evidenced by the peaks in the Fourier transforms at $R \geq 2$ Å. In contrast, for CaMnO₃, the Fourier transform and thus structure are significantly different at 0.2 V.

HERFD-XANES enhances features present in the near-edge region of the absorption spectrum.^{23–25} *In situ* HERFD data and $K\beta$ XES spectra were collected on the I20 Scanning beamline at the Diamond Light Source using a point–point Rowland circle XES spectrometer. Figure 4a,b compares the Mn K-edge HERFD-XANES as a function of potential for LaMnO₃ and CaMnO₃, respectively (data for the reference materials are shown in Figure S8). For LaMnO₃ (Figure 5a), decreasing the potential results in the reduction of Mn as indicated by the shift of the edge position and white line to lower energy, in agreement with the conventional XANES data described above. Two peaks in the pre-edge region arising from t_{2g} and e_g orbitals are identified as A_1 (low energy) and A_2 (high energy) (Figure 5c). Both peaks slightly shift toward lower energies, with the A_2 peak decreasing in intensity more significantly as the potential is made more negative. For CaMnO₃ (Figure 5b), stepping the potential to more negative values results in a more dramatic shift in the Mn edge position by ~ 6 eV toward lower energy. The pre-edge region (Figure 5d) is characterized by a single more intense peak

with a low-energy shoulder at 1.4 and 0.5 V, with only the A_1 peak clearly observed at 0.2 V. As in the case of the conventional XANES spectra, the complex dependency of the pre-edge features on geometry and ligand environment makes further identification of the relative fractions of the Mn species by linear combination fitting to the limited HERFD-XANES reference sample spectra collected inappropriate. However, these data do suggest a stronger potential dependence of the valency and coordination environment of Mn for CaMnO₃ than for LaMnO₃ in agreement with the conventional XAS data.

Further details of the Mn valency can be obtained by analysis of XES, taking advantage of the spin, oxidation state, and ligand sensitivity of the Mn $K\beta$ lines.^{35,36} Figure 5 compares the Mn $K\beta$ XES of LaMnO₃ (a) and CaMnO₃ (b) as a function of the applied potential. The spectra feature a strong $K\beta_{1,3}$ peak and a broad $K\beta'$ shoulder at lower emitted energies due to different 3d spin states.²⁶ Upon changing the potential from 1.4 to 0.2 V, the Mn valence decrease is reflected in the shift of the $K\beta_{1,3}$ maximum to higher energy and accompanied by intensity changes in the $K\beta'$ region. When comparing the spectra with those collected for the reference samples (Figure S9), the *in situ* spectra collected for LaMnO₃ lie in between those for the Mn⁴⁺ and Mn³⁺ references, whereas in the case of CaMnO₃, the spectra lie in between those for Mn⁴⁺ and Mn²⁺.

Previous XES studies have shown that such spectra can be fitted as a linear combination of the $K\beta$ of the constituent cation species.^{37–42} The normalized Mn- $K\beta$ spectra for the reference samples (Figure S9) collected in this study were thus linearly combined to fit the Mn- $K\beta$ spectra for LaMnO₃ and CaMnO₃. Figure 5c,d shows the normalized Mn $K\beta$ spectra for the LaMnO₃ and CaMnO₃ electrodes at the open-circuit potential (OCP, corresponding to 1.9 V) as a combination of the

reference standards (fits for the different potentials can be found in Figure S10 and Table S5, as well as statistics of the fits in Table S6). The results yield an average oxidation state of +3.4 for LaMnO_3 and +4.1 for CaMnO_3 at OCP with the relative fractions of the Mn^{2+} , Mn^{3+} , and Mn^{4+} species shown in Figure S6,f. Application of 1.4 V results in an increase in the Mn^{4+} and decrease in the Mn^{3+} percentage for LaMnO_3 and a corresponding but smaller change for CaMnO_3 . Decreasing the potential to 0.5 V and then to 0.2 V results in conversion of the Mn^{4+} ions to Mn^{3+} for LaMnO_3 , with little change in the percentage of Mn^{2+} . In contrast, the Mn^{4+} ions are observed to be converted to both Mn^{3+} and Mn^{2+} for the CaMnO_3 electrode. As evidenced by the EXAFS data presented above (Figure 4), the perovskite structure is not retained at 0.2 V for CaMnO_3 . Further evidence of this structural change was observed in the *ex situ* X-ray diffraction (XRD) obtained on the dried electrodes after the XES and HERFD-XANES measurements in Figure S11. We propose that it is this over reduction and increase in the fraction of Mn^{2+} that result in the structural changes accompanying the formation of oxygen vacancies.

The implications of the trends in Figure S6,f are crucially important in correlating the intrinsic electrochemical responses of the perovskites and their electrocatalytic activity toward the ORR. As shown in Figure 1, the pseudo-capacitive responses in the LaMnO_3 voltammetric profile coincide with significant changes in XES, confirming that Mn 3d states are being populated/depopulated across the potential range in which the ORR is taking place. On the other hand, the relatively weak changes in the XES features observed in CaMnO_3 across the same potential range suggest that only a fraction of the large pseudocapacitive responses is linked to Mn 3d states. It is not entirely clear which orbitals contribute to the density of states responsible for the pseudo-capacitive responses in CaMnO_3 , although electronic structure calculations by Molinari *et al.* have shown a sizeable density of O 2p states within the band gap of partially reduced CaMnO_3 .⁴³

The tolerance of the catalysts to repeated cycles 1000 times to simulate an accelerated stress test (AST) was further investigated using conventional XAS and XRD (experimental details of AST can be found in the Methods Section and cyclic voltammograms recorded before and after the AST are presented in Figure S12). Figure 6 shows the *ex situ* XANES and Fourier transforms of the EXAFS data collected before and after the AST (fits to the EXAFS data are presented in Figure S13 and fitting parameters in Table S7, with the XRD data shown in Figure S14). All data sets confirm the results from the *in situ* XAS measurements presented above, with the LaMnO_3 undergoing very little structural change, while the perovskite structure is significantly degraded for the CaMnO_3 electrocatalyst. In the case of LaMnO_3 , it can be observed that the perovskite structure is maintained after the AST, with only a slight expansion of the Mn–La distance. In the case of CaMnO_3 , the perovskite structure is no longer observed after the AST, and the Mn–O coordination has changed to tetrahedral (instead of an octahedral). Although the full structure is still unknown, it is highly likely that this is a mixture of different phases. Literature studies on MnO_x thin films exposed to an ORR-relevant potential of 0.7 V *versus* RHE showed the production of a disordered $\text{Mn}_3^{\text{II,III,III}}\text{O}_4$ phase.²⁰

DISCUSSION

Our data show that the pseudo-capacitive responses observed in the voltammograms (Figure 1a) are associated with changes in

the electron population of Mn 3d states in LaMnO_3 which are manifest at the ORR onset potential (Figure 1b). On the other hand, changes in the redox states of Mn sites are observed at a more negative potential in CaMnO_3 , despite a significant pseudo-capacitive current, which is consistent with the lower activity toward the ORR. While *in situ* XANES and HERFD-XANES correspond to a greater fraction of Mn^{3+} for LaMnO_3 than for CaMnO_3 over the potential range for which ORR is observed, further details were obtained from XES (Figure 5). For LaMnO_3 , these measurements showed that Mn^{4+} was found to persist throughout the potential range over which the RRDE measurements were conducted, wherein less of the 2e^- ORR product was observed at the ring than was found for CaMnO_3 . In contrast, the XES data of CaMnO_3 showed that the fraction of Mn^{4+} states significantly decreases at potentials more negative than 0.6 V *versus* RHE. Furthermore, the EXAFS data show that while the Mn–O distance for LaMnO_3 was found to be stable (or even contracting a little) over the potential range, that for CaMnO_3 increased as the potential was made more negative. Such an expansion favors side-on adsorption of O_2 ,¹⁷ and this agrees with the increased fraction of hydroperoxide formed compared to LaMnO_3 .

There has been some suggestions in the literature that oxygen vacancies may participate in the ORR by turning on the bidentate adsorption of O_2 ,⁴⁴ stabilizing the HO_2^- species, which thus yields more of the 4e^- reduction products. For both LaMnO_3 and CaMnO_3 reduction of the Mn ions was found to be accompanied by the formation of oxygen vacancies as evidenced in the EXAFS, evidenced as a decrease in the Mn–O coordination number. The EXAFS results shown in our study suggest that LaMnO_3 is better able to tolerate the formation of these vacancies. In contrast, the EXAFS data suggest that CaMnO_3 is not able to tolerate the formation of oxygen vacancies with the perovskite structure being lost, presumably due to the formation of Mn^{2+} ions and correspondingly greater oxygen loss, which then contributes to the structural collapse of CaMnO_3 observed following accelerated stress testing.

The results presented above demonstrate the added information that may be obtained from a combined approach of *ex situ* and *in situ* X-ray characterization of such electrocatalysts and, in particular, the use of XES to provide details of the relative populations of the various oxidation states, compared to the average oxidation state provided by XANES measurements. The combined use of these techniques has enabled a deeper understanding of the processes observed as the pseudocapacitive response in the voltammetry of these Mn oxides and highlighted the importance of the $\text{Mn}^{4+/3+}$ redox couple in achieving the full 4e^- reduction of oxygen.

METHODS SECTION

Sample Preparation. $(\text{La,Ca})\text{MnO}_3$ perovskite nanoparticles were synthesized employing an ionic liquid-based route described in previous works.^{13,14,29} First, a dispersion of $\text{Mn}(\text{NO}_3)_3$ (0.5 mL, 0.1 M in H_2O) and 0.5 mL of the corresponding A-site metal nitrate (0.5 mL, 0.1 M in H_2O) in 1-ethyl-3-methylimidazolium acetate (1 mL) was prepared and kept under stirring conditions. After heating at 80 °C for 4 h to ensure all water was removed, cellulose (100 mg) was added and the mixture was stirred for 20 min. The gel-like mixture was calcined for 2 h at 700 °C for LaMnO_3 and 850 °C for CaMnO_3 , to ensure single-phase formation.

Material Characterization. XRD patterns were recorded using a Bruker AXS D8 Advance diffractometer with a θ – θ

configuration, using Cu K α radiation ($\lambda = 0.154$ nm). The XRD patterns were refined by the Rietveld method using the FULLPROF program.^{45,46} The following parameters were refined: scale factor, background coefficients, zero-point error, and positional coordinates. The isotropic thermal factors for all the atoms were fixed to a standard value of 1 Å². No cation deficiency was detected, and so, the occupancy factors for both LaMnO₃ and CaMnO₃ were fixed to 1. XRD patterns of the as-synthesized LaMnO₃ and CaMnO₃ oxide nanoparticles can be found in Figure S15 and structural parameters obtained by Rietveld method in Table S8. Transmission electron microscopy (TEM) was performed using a JEOL JEM-1400Plus and representative images for both materials are shown in Figure S16.

Rotating Ring-Disk Electrochemical Measurements. A three-electrode cell was used to conduct the electrochemistry experiments, using a rotating ring-disk electrode (RRDE) fitted to an ALS rotation controller and connected to a CompactStat bipotentiostat (Ivium). The RRDE electrode consisted of a 4 mm glassy carbon disk surrounded by a Pt ring. The collection efficiency was experimentally determined to be 0.4. A graphite rod and a Hg/HgO (in 0.1 M NaOH) were used as counter and reference electrodes, respectively. Measurements were recorded in 0.1 M KOH solution saturated with either purified Ar or O₂. The sample loading (per unit area of the glassy carbon disk) on the electrode surface was 250 $\mu\text{g}_{\text{OXIDE}} \text{cm}^{-2}$, 50 $\mu\text{g}_{\text{VULCAN}} \text{cm}^{-2}$, and 50 $\mu\text{g}_{\text{NAFION}} \text{cm}^{-2}$.

Preparation of Electrodes and *In Situ* XAS and XES Measurements. Button electrodes were prepared by painting the catalyst ink onto a carbon paper support with a loading of 0.5 mg Mn cm⁻². All measurements were collected *in situ*, using our custom-designed electrochemical cells⁴⁷ connected to an Autolab PGSTAT101 potentiostat. Measurements were collected in the N₂-purged 0.1 M KOH electrolyte.

EXAFS measurements were carried out at room temperature at the SAMBA beamline of Soleil Synchrotron (Saclay, France).⁴⁸ The beamline is equipped with a sagittally focusing Si 220 monochromator and two Pd-coated collimating/focusing mirrors to remove higher harmonics. Calibration of the monochromator was carried out using Mn foil, and XAFS spectra were recorded in the fluorescence mode at the Mn K-edge (6539 eV) using a Canberra 35-elements monolithic planar Ge pixel array detector. The spectra were aligned using the Mn foil response. The data were analyzed using the Athena and Artemis softwares.⁴⁹

XES and HERFD-XANES measurements were conducted at Beamline I20-Scanning, of Diamond Light Source,^{50,51} operating with a ring energy of 3 GeV and at a current of 300 mA. The beamline is equipped with an in-house-designed four-bounce scanning Si(111) monochromator, and the harmonic rejection was achieved using two Si-coated mirrors. An X-ray emission spectrometer based on a 1 m diameter Rowland circle operating in the Johann configuration in the vertical plane with three spherically bent Ge(440) analyzers to collect the emission signal was used for the experiment (see Figure S17).⁵² The XES spectra have been normalized with respect to their total area using the range 6465–6497 eV. All the HERFD-XANES measurements were collected at the peak of K $\beta_{1,3}$ line, and nonresonant XES spectra were measured 100 eV above the absorption edge of Mn.

AST Cycling. Studies on the stability of the proposed materials was carried out by performing accelerated stress tests, where the potential was cycled between 1.1 and 0.6 V *versus*

RHE at 0.050 V s⁻¹, during 1000 cycles, following the DOE standard procedures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c00997>.

Percentage of peroxide formation during the ORR; Mn XANES of references; calibration plot for the determination of the average Mn oxidation state from the edge positions; Mn K-edge XANES and k^3 -weighted χ and k^3 -weighted Fourier transform EXAFS data and fits for the pellets; k^3 -weighted χ data and k^3 -weighted Fourier transform EXAFS data and fits for the dry electrodes; k^3 -weighted χ data and k^3 -weighted Fourier transform EXAFS data and fits for the data collected at 1.4 V; k^3 -weighted χ and k^3 -weighted Fourier transform EXAFS data and first shell fits for the data collected at different potentials; HERFD-XANES spectra at the K $\beta_{1,3}$ line of the reference compounds; Mn K β XES spectra of references; linear combination fits of the Mn K β XES spectra of the data collected at different potentials; *ex situ* X-ray powder diffraction measured before and after electrochemistry; cyclic voltammograms of the LaMnO₃ and CaMnO₃ electrodes before and after the AST; k^3 -weighted χ data and k^3 -weighted Fourier transform EXAFS data and fits for the data collected after AST; *ex situ* X-ray powder diffraction measured before and after AST; XRD patterns of the as-synthesized oxides; representative TEM of synthesized oxide nanoparticles; and schematic view of the I20-scanning branch of the Diamond Light Source (PDF)

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Author Contributions

V.C. and A.E.R. conceived the experiments. V.C. synthesized the materials and performed the electrochemistry experiments. V.C.

and D.J.F. analyzed the electrochemical data. EXAFS data were collected by V.C., A.S.L., and D.I. XES and HERFD-XANES data were collected by S.H., A.F., V.C., A.S.L., H.H., and A.E.R. EXAFS, XES, and HERFD-XANES data analyses were performed by V.C. and A.E.R. All authors contributed to the analysis of the results, discussion, and writing and revision of the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Data are available at the University of Southampton data repository, <https://doi.org/10.5258/SOTON/D1810>.

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